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NEW SYNTHETIC ROUTES TO  
BORON CAGE COMPOUNDS

FINAL REPORT  
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  This project was concerned with the development of new synthetic routes to polyhedral boron cage compounds. This work resulted in the development of new synthetic routes to several important classes of compounds, including small cage carboranes, alkenyl-substituted boranes and carboranes, large cage mono-carbon carboranes and multi-cage boranes and carboranes.		

## Summary of Scientific Goals and Results

Polyhedral boron cage compounds have been recognized as having numerous potentially important practical applications due to their unique chemical and physical properties. Unfortunately this potential has been largely unrealized because of the non-selective, low yield synthetic methods required to obtain these compounds. The principle thrust of the work performed under ARO sponsorship was to investigate the fundamental processes involved in the formation of these types of compounds and to apply these techniques to the development of new high yield, low energy, selective synthetic routes.

Our work has demonstrated (1) new catalytic, high yield syntheses of alkenyl boranes and alkenyl carboranes (2) the high yield thermally initiated conversion of alkenylpentaboranes into small cage carboranes (2) new routes to large cage mono-carbon carboranes (3) new catalytic routes to multi-cage compounds and (4) the synthesis of a range of new hybrid cluster systems with unique structural properties.

These results have been described in detail in the publications and progress reports listed below:

### Publications:

1. A.J. Borelli, Jr., J.S. Plotkin and L.G. Sneddon, "Structural Characterization of  $6:4',5'-[(\eta-C_5H_5)Co-2,3-(CH_3)_2C_2B_4H_5][2',3'-(CH_3)_2C_2B_4H_5]$ : A Coupled-Cage Cobaltacarborane Complex Containing a Three-Center Boron Linkage", *Inorg. Chem.*, 21, 1328-1331 (1982).
2. E.W. Corcoran, Jr. and L.G. Sneddon, "Transition Metal Promoted Reactions of Boron Hydrides 4. A One-Step Synthesis of the Coupled Cage Borane,  $1:2'-[B_5H_8]_2$ ", *Inorg. Chem.*, 22, 182 (1983).
3. R.J. Astheimer and L.G. Sneddon, "Pyrolysis Reactions of  $1,5-C_2B_3H_5$  and  $1,6-C_2B_4H_6$ . Isolation of a New Four Carbon Carborane,  $C_4B_7H_{11}$ , and the Boron Carbon Bonded Dimer and Trimers of  $1,5-C_2B_3H_5$ . Improved Synthesis of the Mixed Cage Carborane,  $2':2'[1',5'-C_2B_3H_4][1,6-C_2B_4H_5]$ ", *Inorg. Chem.* 22, 1928-1934 (1983).
4. R.P. Micciche, J.S. Plotkin and L.G. Sneddon, "Structural Characterization of  $3':2-[2',4'-C_2B_5H_6][1,8,5,6-(\eta-C_5H_5)_2Co_2C_2B_5H_6]$ : A Coupled-Cage Cobaltacarborane Containing a Boron-Boron Linkage", *Inorg. Chem.*, 22, 1765-1768 (1983).
5. R.P. Micciche and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 3. Synthesis and Structural Characterization of an Arene-Ferracarborane Complex:  $1-(\eta^6-CH_3C_6H_5)Fe-2,3-(C_2H_5)_2C_2B_4H_4$ ", *Organometallics*, 2, 674-678 (1983).
6. G.J. Zimmerman and L.G. Sneddon, "Structural Characterization of  $1,2$  Dimethyl 3-cyclopentadienylcobalt-2,3-dicarbaoctaborane", *Acta Cryst.*, C39, 856-858 (1983).

7. T. Davan, E.W. Corcoran and L.G. Sneddon, "Transition-Metal-Promoted Reactions of Boron Hydrides 5. Palladium Promoted Pentaborane(9)-Olefin Coupling Reactions: A New, Mild Synthetic Route to Alkenylpentaboranes", *Organometallics*, 2 1693-1694 (1983).
8. J.A. Anderson, R.J. Astheimer, J.D. Odom and L.G. Sneddon, "The Use of Nuclear Magnetic Resonance to Investigate Bonding Between Quadrupolar Nuclei. Boron-Boron Spin-Spin Coupling Constants in Linked Polyhedral Borane and Carborane Cages", *J. Amer. Chem. Soc.*, 106, 2275-2283 (1984).
9. R.J. Astheimer and L.G. Sneddon, "Photochemical Reactions of Hexafluoroacetone with Pentaborane(9) and 2,4-Dicarbaheptaborane(7)", *Inorg. Chem.* 23, 3207-3212 (1984).
10. R.J. Micciche, J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 4. Direct Synthesis of ( $\eta^6$ -Arene)Ferracarborane Clusters From Alkynes and Boranes. Structural Characterization of Four Carbon ( $\eta^6$ -Arene)Metallacarboranes: 1-[( $\eta^6$ -(CH<sub>3</sub>)<sub>6</sub>C<sub>6</sub>)Fe-4,5,7,8-(CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>5</sub>H<sub>3</sub>] and 2-[( $\eta^6$ -CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>)Fe-6,7,9,10-(CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>5</sub>H<sub>3</sub>]. *Organometallics*, 3, 1396-1402 (1984).
11. R.J. Micciche, J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 5. Synthesis of the First ( $\eta^6$ -Arene)Metallaborane and ( $\eta^6$ -Arene)Metallaioxaborane Clusters. Structural Characterizations of 5-[( $\eta^6$ -C<sub>6</sub>(CH<sub>3</sub>)<sub>3</sub>H<sub>3</sub>)FeB<sub>7</sub>H<sub>13</sub>] and 2-[( $\eta^6$ -C<sub>6</sub>(CH<sub>3</sub>)<sub>3</sub>H<sub>3</sub>)Fe-6-OB<sub>8</sub>H<sub>10</sub>]. *Inorg. Chem.* 23, 3992-3999 (1984).
12. E.W. Corcoran, Jr. and L.G. Sneddon, "Transition Metal Promoted Reactions of Boron Hydrides 6. Platinum(II) Bromide Catalyzed Borane and Carborane Dehydrodimerization Reactions: A New Synthetic Route to Boron-Boron Linked Multi-Cage Boranes and Carboranes" *J. Amer. Chem. Soc.* 106, 7793-7800 (1984).
13. J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 6. Synthesis and Structural Characterization of a Coupled Diborane-Metallacarborane Cluster: 5:1',2'-[1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-2,3-(Me<sub>3</sub>Si)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>][B<sub>2</sub>H<sub>3</sub>]" *Organometallics*, in press.
14. R.J. Micciche, P.J. Carroll and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 7. Synthesis and Structural Characterization of an Open-Cage Triple-Decker Metallathiorborane Cluster 4,6-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>-Co<sub>2</sub>-3,5-S<sub>2</sub>B<sub>2</sub>H<sub>2</sub>" *Organometallics*, submitted.
15. J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 8. Synthesis of New Iron, Cobalt and Nickel Clusters Derived From 2,6-C<sub>2</sub>B<sub>7</sub>H<sub>11</sub>. Structural Characterizations of 2-[( $\eta^6$ -C<sub>6</sub>(CH<sub>3</sub>)<sub>3</sub>H<sub>3</sub>)Fe-1,6-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub>], 6-[( $\eta^6$ -C<sub>6</sub>(CH<sub>3</sub>)<sub>3</sub>H<sub>3</sub>)Fe-9,10-C<sub>2</sub>B<sub>7</sub>H<sub>11</sub>] and 5,7,8-(CH<sub>3</sub>)<sub>3</sub> 11,7,8,10 [( $\eta^3$ -C<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>H)NiC<sub>3</sub>B<sub>7</sub>H<sub>7</sub>] in preparation.

# Progress Reports

## No.

1. 1/1/82-6/30/82
2. 7/1/82-12/31/82
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